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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF COMPLEX CHROMIUM-CONTAINING SILICON AND BORON OXIDES

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Complex chromium-containing oxides, namely, chromium orthoborate and chromium(II) silicate, are synthesized in one-stage combustion using solid oxidizers.

The first products synthesized using self-propagating high-temperature synthesis (SHS) were powders of high-melting compounds, namely, boron nitrides and carbides, titanium and molybdenum silicides, etc. (USSR Inventor's Certif. No. 255221). Their successful use in powder metallurgy for sintering, isothermal spray deposition, and especially in abrasive engineering stimulated further technological evolution of SHS. Borides and silicides are produced on the basis of mixtures of low-dispersion boron and silicon powders with respective metal powders. However, the production of boron and silicon compounds appears promising as well with respect to the synthesis of complex oxide materials, which are characterized by high thermal stability and the absence of phase transformations at a temperature of about 1000°C. The present paper demonstrates the possibility of SHS of complex chromium-containing silicon and boron oxides, namely, $SiCr_2O_4$ (chromium(II) silicate) and $BCrO_3$ (chromium orthoborate).

The combustion process was implemented in mixtures previously subjected to mechanical activation (a planetary mill made by FRITSCH, Germany; corundum containers and balls; duration 2 h), which consisted of metallic chromium powder PKhM-1 mixed with chromium(III) oxide, boron(III) oxide, or silicon(IV) oxide. In order to ensure the balance of oxygen in the reaction, sodium perchlorate powder (a solid oxidizer) was additionally introduced into the mixtures, according to the following schemes:

$$Cr + 0.5\ Cr_2O_3 + B_2O_3 + 0.375\ NaClO_4 \rightarrow 2BCrO_3 + 0.375\ NaCl; \quad (1)$$

$$Cr + 0.5\ Cr_2O_3 + SiO_2 + 0.125\ NaClO_4 \rightarrow SiCr_2O_4 + 0.125\ NaCl. \quad (2)$$

It should be noted that due to the existence of a significant temperature gradient in the course of combustion, up to 80% sodium chloride is sublimated in the course of the reaction. The remaining salt can be easily removed using distilled water or organic solvents.

Published data on chromium borates and silicates are scarce. Certain structural characteristics and properties of chromium orthoborate are presented in [1 – 3] and those of chromium silicate in [4, 5]. The characteristics of the SHS products, namely $BCrO_3$ and $SiCr_2O_4$, are given in Table 1. The x-ray phase analysis was carried out on a DRON-3M device (CuK_α radiation, Ni filter); the pycnometric densities were determined based on the standard method using toluene.

The data on the unit cell parameters of boron and silicon compounds virtually agree with the results in [2] and [4], respectively, whereas the pycnometric density of chromium

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TABLE 1

Product	Pycnometric density, g/cm^3	Unit cell parameters				Weight content, %					
						B		Cr		Si	
		a, Å	*b*, Å	*c*, Å	*V*, Å^3	estimated	found by analysis	estimated	found by analysis	estimated	found by analysis
$BCrO_3$*	3.78	4.477	–	14.534	252.3	9.76	9.60	46.92	45.55	–	–
$SiCr_2O_4$**	3.70	5.597	11.379	9.307	592.7	–	–	53.04	52.80	14.32	13.50

* Rhombic syngony.

** Orthorhombic syngony.

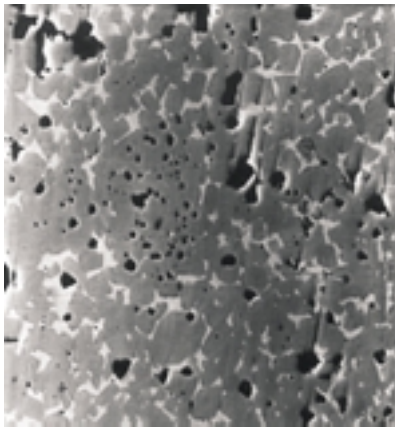

Fig. 1. Microstructure of $BcrO_3$ that is a product of SHS (COMPO photo, × 1000).

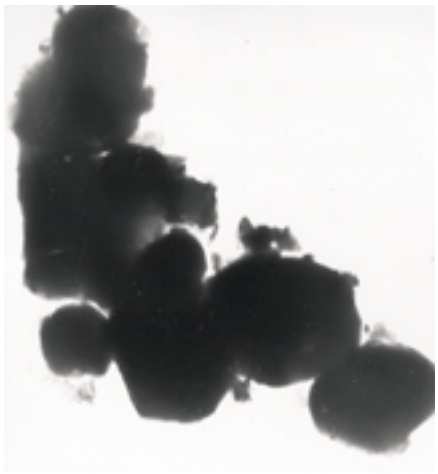

Fig. 2. Photomicrograph of particles of $SiCr_2O_4$ that is a product of SHS (× 17,000).

orthoborate that is a product of SHS is somewhat lower than the value obtained in [2] for the material synthesized according to the traditional technology (4.27 g/cm^3), due to the higher porosity of SHS products, which is related to substantial gas release in combustion of the reactant mixtures. This is substantiated by the data on the microstructure of the products (Fig. 1). The photomicrographs made with scanner electron microscopes reveal the presence of particle agglomerates in the products of synthesis, whose average estimated size is about 1 μm (Fig. 2). The diffraction patterns obtained by the electron diffraction method corroborate the formation of polycrystalline structures in the SHS products (Fig. 3). The distribution of elements in the reaction products in both systems (a JEM 733 JEOL electron microscope, Japan) is demonstrated in Fig. 4. The elements are distributed in the products of synthesis with a high degree of homogeneity.

Thus, complex chromium-containing oxides, namely, chromium orthoborate and chromium(II) silicate have been synthesized in one-stage combustion using solid oxidizers. As distinct from the traditional synthesis in a furnace, this technology is faster and more efficient.

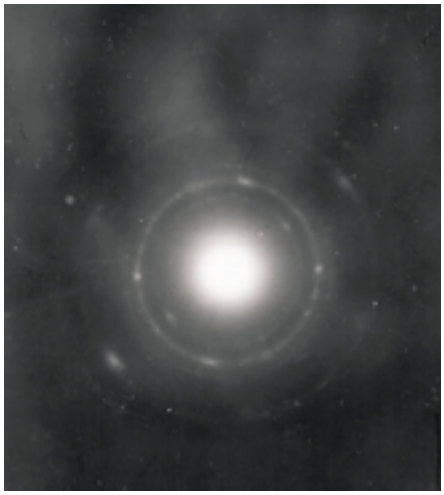

Fig. 3. Diffraction pattern of $BCrO_3$ that is a product of SHS (× 80,000).

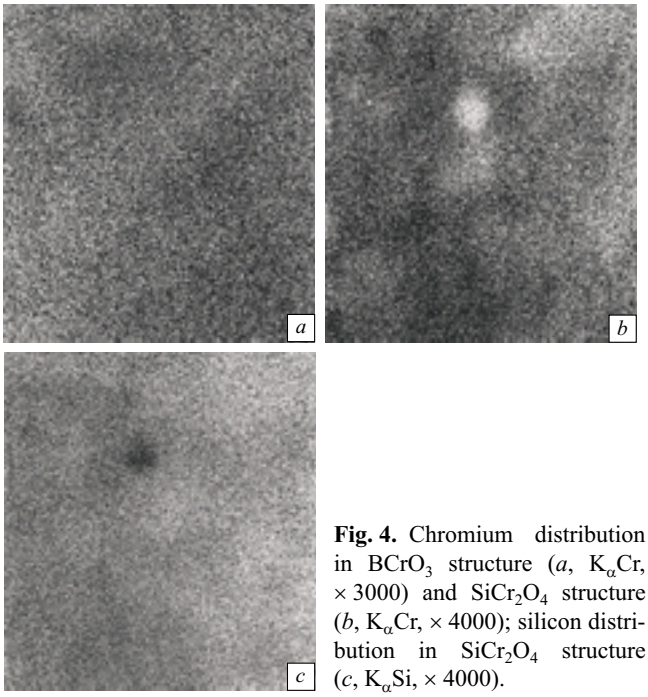

Fig. 4. Chromium distribution in $BCrO_3$ structure (*a*, $K_\alpha Cr$, × 3000) and $SiCr_2O_4$ structure (*b*, $K_\alpha Cr$, × 4000); silicon distribution in $SiCr_2O_4$ structure (*c*, $K_\alpha Si$, × 4000).

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